

Evaporation Effects on Oxygen and Hydrogen Isotopes in Deep Vadose Zone Pore Fluids at Hanford, Washington

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ABSTRACT

Stable isotopes of O and H were measured in pore fluid extracted from a sediment core located in a relatively undisturbed area in the Hanford site near the S-SX Tank Farms. Pore fluids from most of the 70-m-thick vadose zone section have $\delta^{18}\text{O}$ values that are shifted to higher values than those for winter precipitation (and Columbia River water) by 3 to 4‰. The shift of $\delta^{18}\text{O}$ and the $\delta^{18}\text{O}$ - δD slope of about 4 in the deep vadose zone pore fluids is attributed to partial evaporation during residence in the upper meter of the soil section. A model relating the isotopic shift to recharge and soil properties suggests that the shift should be inversely proportional to recharge, and larger for coarser soils with lower water retention. When applied to Hanford soils and precipitation patterns, the model predicts that vadose zone pore fluids at Hanford should typically be shifted by +2 to +6‰ in $\delta^{18}\text{O}$ relative to the values in wet season precipitation, even for relatively high values of annual net infiltration (up to 100 mm yr⁻¹ or 60% of annual precipitation). The model has implications for groundwater as well as vadose zone $\delta^{18}\text{O}$. The effects of vegetation are not included, so only upper limit values for the net infiltration flux can be inferred from vadose zone $\delta^{18}\text{O}$. The shifted $\delta^{18}\text{O}$ of natural pore fluids allows identification of the presence of subsurface water that comes from industrial discharges at the Hanford site. An example is provided by a low $\delta^{18}\text{O}$, high water content horizon at a depth of 44 m in the core, which is interpreted as industrial water that was transported laterally above a capillary barrier as a result of a nearby, near-surface point discharge that happened within the past 50 yr.

ESTIMATING DIFFUSE RECHARGE through the thick vadose zones of arid and semiarid regions has presented a challenge for decades. Where the net infiltration flux is small, it is particularly difficult to quantify the value because of the sensitive dependence of hydraulic conductivity on water content in unsaturated soils, especially at small water contents (e.g., van Genuchten, 1980). Seasonal variations in temperature and the volume and nature of precipitation also affect the amount of water available for deep infiltration. The kinds of soils and vegetation in near-surface layers strongly influence whether the moisture is recycled to the atmosphere through evapotranspiration or able to migrate into the deeper subsurface (e.g., Gee et al., 1994; Newman et al., 1997; Gee and Ward, 2002).

At the Hanford site in south-central Washington, where large amounts of radionuclides have been released to the vadose zone, determination of the natural net infil-

tration flux is important, because the future downward transport of the resident inventory of radionuclides depends on the fluid flow available to facilitate transport. Methods that provide long-term average values of net infiltration flux are of particular value for predicting transport in the next hundreds to thousands of years.

Chemical methods for estimating vadose zone net infiltration flux include Cl^- mass balance and detection of bomb-pulse radionuclides like T, ^{129}I , and ^{36}Cl . Stable hydrogen (δD) and oxygen ($\delta^{18}\text{O}$) isotopic compositions of vadose zone water may also provide information on net infiltration (e.g., Zimmerman et al., 1967; Barnes and Allison, 1983, 1984, 1988; Shurbaji et al., 1995; Melayah et al., 1996; Phillips, 1994; Allison et al., 1994; Liu et al., 1995; Newman et al., 1997). A broadly accepted formula for translating O and H isotopic data into net infiltration fluxes has not been forthcoming. A semi-empirical approach was proposed by Barnes and Allison (1988), but there have been few followup studies to demonstrate its generality.

In this paper, we present data on the H and O isotope composition of pore water extracted from core samples from a borehole drilled in the 200 West area at the Hanford site in south-central Washington. The vadose zone at this site is about 70 m thick and the pore fluids show systematic shifts in O and H isotopic compositions relative to the values of precipitation and groundwater. The shifted water isotopic values are interpreted using an approximate, one-dimensional model for the vadose zone water transport. This model treats unvegetated sites, and relates the mean delta values of deep vadose zone pore fluids to the average near-surface soil moisture content and average annual net infiltration flux or drainage. Because vegetation tends to decrease drainage without changing the water isotopic composition, the model indicates that $\delta^{18}\text{O}$ measurements can provide only upper limits for drainage at vegetated sites. The one-dimensional assumption may not be applicable to some arid zone sites where fractures are important, but is reasonable in this case because the Hanford vadose zone is composed of unconsolidated sediments. The results show that natural vadose zone fluids at Hanford should be isotopically shifted relative to precipitation and therefore also distinct from the Columbia River water that was, and continues to be, used for industrial operations. Therefore the O and H isotopic data can be used not only to measure infiltration conditions, but also to identify subsurface water that comes from water line leaks, spills, and purposeful flooding at the surface.

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Abbreviations: CIG, Center for Isotope Geochemistry; GMWL, Global Meteoric Water Line; LBNL, Lawrence Berkeley National Laboratory (LBNL).

HANFORD SITE GEOLOGY AND HISTORY

The Hanford site is located in the Pasco Basin in south-central Washington approximately 10 km north of the confluence of the Columbia and Yakima rivers (Fig. 1). The location of Borehole 299-W22-48 is in the 200 West area in the central part of the site. There is considerable radionuclide contamination in the vadose zone in the 200 areas. From 1950 through 1986, the 200 West area was used for processing Pu for nuclear weapons. High-level radioactive waste generated from these activities is stored in tanks, several of which have leaked, in the 200 West and 200 East areas. Low-level waste was also discharged directly to the ground through infiltration ponds and cribs (buried, open-bottomed containers).

The subsurface geology of the Hanford site consists of sedimentary deposits overlying Miocene tholeiitic basalt flows of the Columbia River Basalt Group. The basalts are gently folded and faulted to form broad basins, including the Pasco Basin (Reidel, 1998). Unconformably overlying the basalt is the Pliocene Ringold formation, which consists of fluvial deposits of gravel, silt, and clay. In the Hanford area, the Ringold is separated into coarser gravel-sand units and fine-grained silt-mud units (Reidel et al., 1994). The Ringold formation is unconformably overlain by the late Pliocene Cold Creek unit [CCUc-f(calc)], which consists of alluvial deposits and soil horizons cemented by pedogenic carbonate (USDOE, 2002). Above the CCUc-f(calc) unit is the highly stratified fine-grained sand and silt facies of the CCUf(lam-mas). Within the 200 West Area these distinct facies are often referred to as the lower and upper Cold Creek Units, respectively.

The Hanford formation, the uppermost geologic unit in the 200 Area plateau, consists of alluvial sediments deposited by cataclysmic floods caused by collapse of ice dams on the upper part of the Columbia River drainage during the Pleistocene period. The thickness of the Hanford formation is variable, up to 100 m. The age of the Hanford formation was originally believed to be restricted to late Wisconsin (12–16 ka), but recently reported radiometric and paleomagnetic data suggest that it was deposited episodically throughout the Pleistocene (Bjornstad et al., 2001) and hence may be as old as 2 million years at its base.

During the Pleistocene flood events, water collected briefly in the Pasco basin and then, within about 5 d, drained through the Wallula Gap (Allison, 1933). Gravel-rich units formed in high-energy channels. Adjacent to the main channels, thick sequences of coarse-to fine-grained sands were deposited. Rhythmic graded beds consisting primarily of silt with minor sand, and ranging from 0.1 to 1 m thick were formed in slack water areas (Baker et al., 1991). The Hanford sediments are also intruded by clastic dikes and sills, which formed when trapped water was expelled from the more deeply buried flood deposits along vertical channels shortly after deposition. The clastic dikes tend to have higher concentrations of fine-grained material and have a significantly lower hydraulic conductivity than the surrounding sediments (Murray et al., 2001).

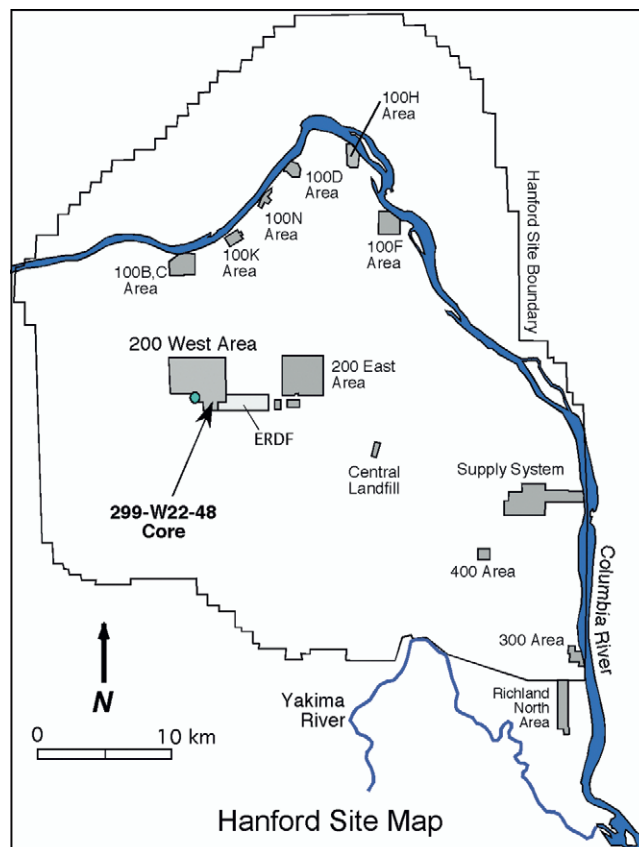


Fig. 1. Map of the Hanford site showing the location of the study site in the southeast part of the 200 West area.

SAMPLING AND ANALYTICAL METHODS

Drilling, Core Sampling, and Stratigraphy

During October of 1999, Borehole 299-W22-48 was drilled in a relatively undisturbed section of the 200 West area to provide background data on the geologic, hydrologic, and chemical properties of the sediments in this area (Fig. 1). Relatively undisturbed in this case means that no significant structures are on the site, and there has been no excavation and/or backfilling at the site. However, the site is only about 100 m east of the edge of the S-SX Tank Farm and therefore may have been disturbed by vehicle traffic and other activities at the time of the S-SX Tank Farm construction. The drill site was chosen for study because the S-SX tank farm is known to have several leaking tanks. Before drilling the borehole, the vegetation at the site was removed and a drilling pad constructed. Anecdotal evidence suggests that the vegetation in the vicinity of the borehole had been disturbed before drilling the hole (J.C. Evans, personal communication, 2002), probably at the time the Tank Farm was constructed. The details of vegetation removal remain uncertain. The interpretations given below assume that the 299-W22-48 site had shrub-steppe vegetation (e.g., sagebrush, rabbitbrush, bunchgrass mixture) until about 1950 and thereafter has been without significant vegetation due to Hanford Site operations.

The 299-W22-48 core was drilled with a 25-cm (10-in) outer diameter hollow stem auger. Core samples were collected by removing the bit on the auger and driving a 7.6-cm (3-in) inner diameter, 0.6-m (2-ft) long split spoon sampler into the undisturbed sediments beneath the auger. The split spoon sampler included four 15-cm (6-in) Lexan liners (GE Plastics, Pittsfield, MA). After the sampler was retrieved, the Lexan

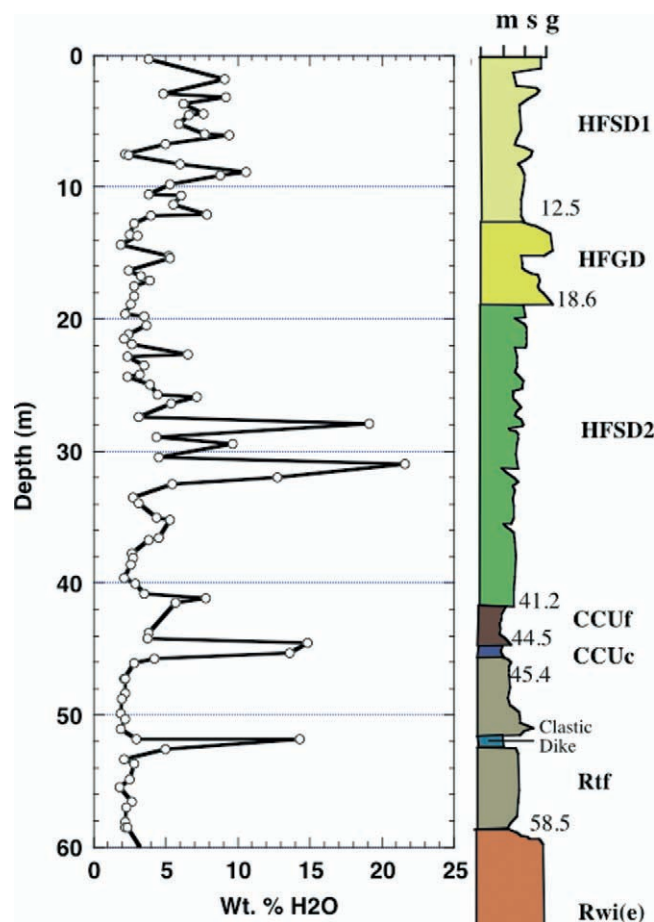


Fig. 2. Water contents of sediment samples from the 299-W22-48 core. Right side of graph shows the lithologic column, with the thickness of the column representing the relative proportions of fine and coarse material (m: mud, s: sand, g: gravel). HFSD: Hanford Formation, gravel-dominated facies; HFSD2: Hanford Formation, sand-dominated facies; CCUf(lam-msv): Cold Creek unit, silt and fine-grained sand; CCUc-f(calc): Cold Creek unit, calcic paleosol; Rtf: Ringold Formation, upper fines; Rwi: Ringold Formation, sandy gravel. Data from Serne et al. (2002b) and USDOE (2002).

liners were removed from the sampler and capped at both ends. The auger bit was replaced and advanced to the next interval to be sampled.

The cores were kept sealed and refrigerated until they could be subsampled for analysis. For the samples collected in Lexan sleeves, the sleeves and caps were cut longitudinally, and the core split down the middle. To minimize evaporation, samples for measurements of the isotopic compositions of the pore waters were collected from the central part of the sampled interval immediately after the core was split open. Approximately 200 g of material for isotopic analyses was placed into a wide-mouthed, plastic sample bottle and sealed.

The stratigraphic column on the right-hand side of Fig. 2 summarizes the geology of the core. The upper 41 m of the core are in the Hanford formation. At this location, the Hanford formation has been subdivided into three informal facies associations. The HFSD1 unit extends from the surface to 12.5 m depth and is made up of fine- to medium-grained silty sands. The HFSD unit, between 12.5 and 18.5 m depth, is a coarser-grained sand and gravel-dominated facies. From 18.5 to 41 m depth is the lower HFSD2 unit that is similar in texture to the upper sand-dominated unit. Beneath the Hanford formation is a 3-m-thick section of the CCUf(lam-mas) facies, underlain

by the 1-m-thick carbonate-rich lower Cold Creek unit (CCUc-f(calc) (Slate, 1996). Beneath the Cold Creek unit is the Ringold formation. The top 13 m of the Ringold is a fine-grained unit consisting of muds and sands. Within this unit, at a depth of approximately 52 m, is a clastic dike. Beneath the fine-grained unit, extending to the bottom of the borehole, is a coarse sand and gravel unit.

Pore Water Extraction

The pore water in the samples collected for isotope analyses (δD and $\delta^{18}O$) was vacuum-distilled from the samples at 100°C at the Center for Isotope Geochemistry (CIG) at the E.O. Lawrence Berkeley National Laboratory (LBNL). The water contents of the samples were determined by weighing the samples before and after the water was extracted, and dividing the difference by the total weight of the wet sample.

The water contents determined by the vacuum-distillation method are in very good agreement with those determined by oven drying the samples. Where the water contents of splits of the same sample were measured by both methods, the results were generally within $\pm 10\%$ of each other. Most of this variability is believed to be the result of the heterogeneity of the samples. Quantitative recovery of water from the sample is critical for the isotope analyses, as it has been shown that yields of $< 98\%$ of the total water in a sample can lead to significant shifts in the isotopic composition of the water (Araguás-Araguás et al., 1995).

δD and $\delta^{18}O$ Analyses

The stable isotope compositions of the water samples were analyzed at CIG's LBNL labs. The H isotope ratios of the waters were analyzed using the method of Vennemann and O'Neil (1993). Three-microliter water samples were injected into evacuated Pyrex tubes containing approximately 50 mg of zinc metal. The water was reduced to H_2 gas by baking the tubes for 20 min at 500°C. The H isotope ratios of the H_2 gas were analyzed using the VG Instruments Prism Series II isotope ratio mass spectrometer at the Lawrence Berkeley National Laboratory. The $\delta^{18}O$ values of the samples were analyzed using an Isoprep automated CO_2 - H_2O equilibration system interfaced to the Prism. The isotope ratios are expressed as per mil deviations from an internationally accepted standard (V-SMOW). For H, duplicate analyses of the δD values of the waters were generally within $\pm 2\%$. For O, the precision of the measurements is $\pm 0.1\%$.

RESULTS

Moisture Content of Sediments

The moisture contents of the sediments in 299-W22-48, measured by neutron logging of the borehole (Serne et al., 2002b), are plotted in Fig. 2. These moisture contents were originally reported as percentage of water (v/v), but have been converted to percentage of water (w/w) for comparison with our results. Volumetric water contents are 1.8 times higher than the values shown. In general, the moisture contents are < 0.1 , but there are a few notable areas with high water content. In the lower part of the core, both the clastic dike zone and the lower Cold Creek unit had moisture contents above 0.15 ($\theta \approx 0.27$). In the HFSD2 unit of the Hanford formation, there are two zones at approximately the 30-m depth with moisture contents up to 0.2 ($\theta \approx 0.36$).

Table 1. Water content and O and H isotope data for soil samples from Core 299-W22-48, Hanford Site.

Sample	Depth		Dry weight g	Water† %	$\delta^{18}\text{O}$	δD	$^3\text{H}\ddagger$ pCi L ⁻¹
	m	ft					
1	0.38	1.0–1.5	193.9	4.4	–9.1	–100	628
2	1.91	6.0–6.5	202.1	7.9	–16.8	–134	
3	2.97	9.5–10.0	229.6	6.8	–14.9	–122	8885
4	4.50	14.5–15.0	188.7	6.6	–14.6	–129	450
5	6.02	19.5–20.0	205.5	6.1	–14.5	–125	458
6	7.54	24.5–25.0	192.7	2.1	–14.6	–125	
7	9.07	29.5–30.0	217.0	7.6	–14.7	–124	339
8	10.59	34.5–35.0	202.4	3.0	–14.4	–126	516
9	12.12	39.5–40.0	220.9	5.7	–14.4	–121	916
10	13.64	44.5–45.0	242.0	2.5	–13.0	–114	2113
11	15.32	50.0–50.5	185.6	4.8	–14.7	–121	459
12	17.15	56.0–56.5A	226.6	3.5	–14.1	–122	450
13	17.15	56.0–56.5B	226.2	3.3		–124	619
14	17.60	57.5–58.0	217.1	2.8	–13.5	–121	601
15	18.97	62.0–62.5	182.7	1.9	–12.8	–115	
16	21.26	69.5–70.0	178.3	1.7	–14.6	–121	
17	24.31	79.5–80.0	163.8	2.4	–14.2	–120	968
18	26.37	86.5	152.4	4.3	–14.7	–127	635
19	29.41	96.5	165.6	9.1	–15.1	–130	1037
20	32.61	106.5–107.5	177.2	2.8	–14.9	–131	
21	36.73	120.5	160.8	3.7	–14.5	–126	
22	37.95	124.0–125.0	173.7	3.2	–14.8	–125	
23	38.71	126.5–127.5	170.7	2.9	–14.4		
24	44.65	146.0–147.0	154.7	16.5	–17.3	–145	1284
25	45.42	148.5–149.5	163.0	7.7	–14.6	–125	757
26	46.18	151.0–152.0	174.2				
27	49.99	163.5–164.5	186.4	2.1	–14.4	–127	
28	51.21	167.5–168.5	153.7	9.1	–14.9	–127	
29	51.97	170.0–171.0	168.4	3.0			
30	53.80	176.0–177.0	190.6	2.6	–15.4	–127	
31	57.15	187.0–188.0	166.2	2.4	–13.6	–130	
32	71.78	235.0–236.0	160.1	10.6	–16.9	–130	

† Water content is given in units of milliliters per gram of dry sediment.

‡ Where no number is given, concentration is below detection limit.

The high water contents are associated with finer-grained sedimentary layers. The upper 12 m of the core has water contents that are significantly higher than those of lower sections with similar grain size. This may be an indication of higher drainage rates in the recent past (10–50 yr depending on the rate). The sample at 0.38 m has $\theta \approx 0.07$.

Water contents were also measured for 30 samples in conjunction with the measurements of δD and $\delta^{18}\text{O}$ (Table 1), using the water vapor yield of the vacuum extraction method. The isotope samples from 29.4, 44.7, and 51.2 m, which correspond to the silt layers in the Hanford formation, the lower Cold Creek unit caliche layer, and a clastic dike in the Ringold formation, all have high water contents, as does a sample taken beneath the water table at 71.8 m depth.

Stable Isotope Composition of Vadose Zone Pore Waters

The $\delta^{18}\text{O}$ and δD values of 30 extracted pore water samples were measured (Table 1). The $\delta^{18}\text{O}$ values of the pore water samples are plotted against their δD values on Fig. 3. Also shown on this figure are the Global Meteoric Water Line (GMWL) and data on local Hanford precipitation from 1982 and 1983 cited by Hearn et al. (1989) (data source is Basalt Waste Isolation technical report BWI-DP-061). The precipitation at Hanford varies seasonally. Winter precipitation tends to have the lower delta values ($\delta^{18}\text{O} \leq -16$), and for plots close to the GMWL. Summer precipitation has

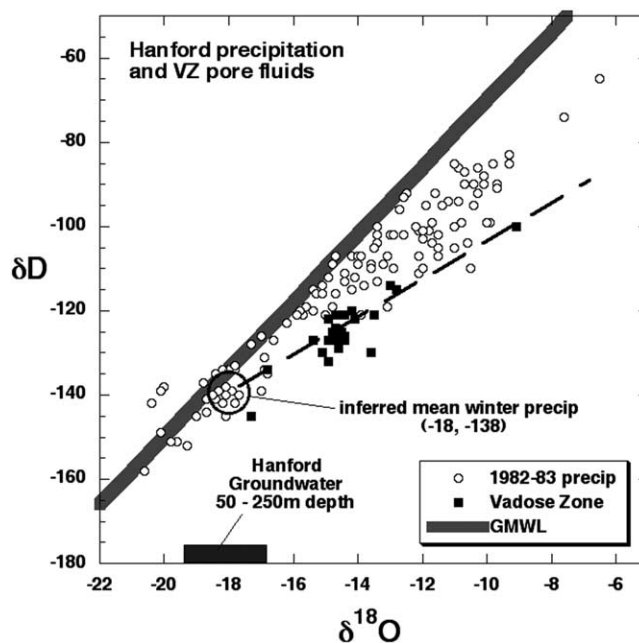


Fig. 3. δD vs. $\delta^{18}\text{O}$ values for the vadose zone pore waters extracted from the 299-W22-48 core. Also shown are the global meteoric water line, local precipitation values (Hearn et al., 1989; data from BWI-DP-061), and the range of $\delta^{18}\text{O}$ values for shallow groundwater from Hearn et al. (1989). The estimated mean value for winter precipitation, which provides the bulk of infiltrated water, is shown by the circle and corresponds to $\delta^{18}\text{O} = -18 \pm 0.5$ and $\delta\text{D} = -138 \pm 4$. Deep vadose zone waters have $\delta^{18}\text{O}$ values that are 2.5 to 5‰ higher than mean winter precipitation. The highest $\delta^{18}\text{O}$ value is from the sample at the 38-cm depth in the core. The slope of the best fit line through the vadose zone data is 4.9, which is significantly lower than the value for the meteoric water line (approximately 8), but higher than the values measured by Allison and Barnes (1993) in experiments on evaporating soil columns (close to 3).

higher $\delta^{18}\text{O}$ and is shifted to the right of the GMWL, indicating that precipitation is affected by nonequilibrium evaporation in the dry summer season, which is common in arid regions (Gat, 1996). The line defined by the pore fluids has a slope of approximately 5, considerably smaller than the slope of 8 of the GMWL. The lower slope trend is typical of waters that have undergone evaporation in air with low relative humidity (e.g., Gat, 1996; Gaye and Edmunds, 1996). The slope of the δD – $\delta^{18}\text{O}$ line is strongly controlled by the high $\delta^{18}\text{O}$ point and hence has a substantial uncertainty, but it is nevertheless clear that the bulk of the pore fluid data fall below the meteoric water line and hence have isotopic compositions that reflect the effects of evaporation into undersaturated air. The majority of the vadose zone pore fluids have values between -15.5 and -12.8 ‰; excluding the extreme high value the average value is -14.4 ± 0.6 (1 σ).

The O isotope data for the pore waters are plotted against depth in Fig. 4. The $\delta^{18}\text{O}$ values of the two shallowest samples (0.38- and 1.9-m depth) are significantly different from the deeper samples. The 0.38-m depth sample is strongly enriched in ^{18}O , whereas the 1.9-m depth sample has a low $\delta^{18}\text{O}$ value. This pattern is similar to results from other studies of shallow, unsaturated soils (Komor and Emerson, 1994; Phillips, 1995; Mel-

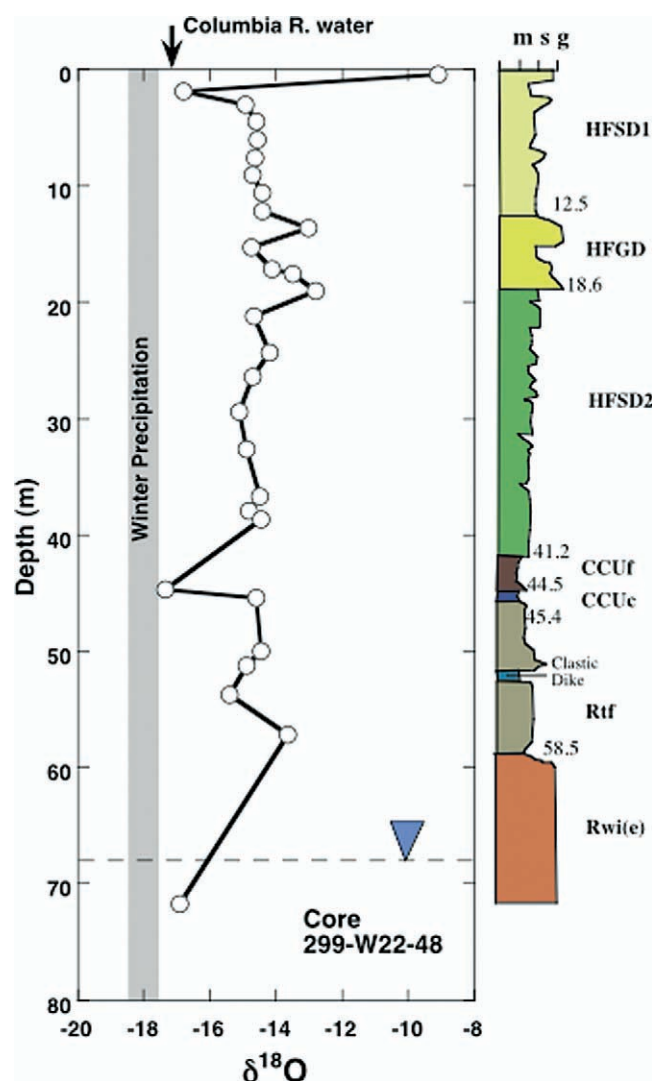


Fig. 4. $\delta^{18}\text{O}$ vs. depth for the 299-W22-48 pore water samples. The stratigraphic units given on Fig. 2 are also shown, along with the approximate groundwater level and the average O isotopic composition of winter precipitation and Columbia River water (the water used for Hanford operations).

ayah et al., 1996; Barnes and Allison, 1988). We interpret the values of the 1.9-m depth sample (-16.8 , -134) as upper limits for the isotopic values for the previous major precipitation event. The shallowest sample has been strongly affected by evaporation.

Beneath 2 m, most of the pore waters are in a restricted range, with only one exception. Within the Hanford formation, the isotopic compositions of 20 samples were analyzed. In the finer-grained sediments of the HFSD1 and HFSD2 units, the isotopic compositions of the pore waters are remarkably consistent ($\delta^{18}\text{O}$ values of -14.2 to -15.1 ‰, averaging -14.6 ‰). In the coarser sediments of the HFGD unit, the $\delta^{18}\text{O}$ values are more variable and have a higher average value (-13.6 ‰).

The pore water from only one sample of the upper Cold Creek unit, the high water content sample from above the caliche layer at 44.6 m, was analyzed. The $\delta^{18}\text{O}$ value (-17.3 ‰) is significantly lower than the pore water in the overlying sediments and is in the range of

Columbia River water and groundwater (Fig. 3). Clearly, this water is not derived from direct, vertical infiltration in the vicinity of the borehole. Slightly elevated levels of NO_3 , Cr, Tc, and T were detected in this sample (Serne et al., 2002a, 2002b). Our interpretation is that this water was derived from nearby Hanford operations and entered the region of the borehole by horizontal migration. The most likely sources of this water are the 216-S3 cribs located approximately 50 m WNW of the borehole. It is also possible that there could be some input from the 241-S tank farm, but that would probably have been small given the relatively low concentrations of radionuclides in the water.

The O isotopic compositions of the pore waters extracted from the underlying Ringold vadose zone samples also indicate that they were affected by evaporation. The range of $\delta^{18}\text{O}$ values for these samples (-13.6 to -15.4 ‰) is slightly larger than that observed for the finer-grained units of the Hanford formation, but the average value is the same (-14.6 ‰). The deepest sample in the borehole is from the saturated zone and has a $\delta^{18}\text{O}$ value (-16.9 ‰) close to the average for groundwater samples recently collected from monitoring wells in the area (Singleton et al., 2003).

DISCUSSION

$\delta^{18}\text{O}$ Value of Wet Season Precipitation at Hanford

The pore water values are shifted to higher $\delta^{18}\text{O}$ values than those of infiltrating precipitation at the Hanford site, but there is some uncertainty as to exactly how much. Available data for precipitation at the Hanford site are shown in Fig. 3 (from BWI-DP-061). The data are not especially well documented with regard to time of year and precipitation amount, but we infer that the lower values of $\delta^{18}\text{O}$ are those for winter precipitation. The samples with high values are presumably precipitation events in late spring through early fall when humidity is low and evaporation effects are significant. The average values for $\delta^{18}\text{O}$ and δD for the samples with $\delta^{18}\text{O}$ less than -16 is -18.2 and -139 , respectively. We propose that these values are close to an average for winter precipitation. Other available data are consistent with this inference. The $\delta^{18}\text{O}$ value of water from the 1.9-m core sample (-16.8) is a direct measure of local infiltration, but probably an upper limit due to effects of evaporation. Data presented by Hearn et al. (1989) show that groundwater sampled in Hanford wells from the upper aquifer (above about 250 m depth below ground surface) has $\delta^{18}\text{O}$ values between -16.8 and -19.5 . These values may also be slightly affected by evaporation, but they are roughly consistent with an average winter precipitation $\delta^{18}\text{O}$ value of about -18 . Taking the average winter precipitation to have $\delta^{18}\text{O} = -18 \pm 0.5$ and $\delta\text{D} = -138 \pm 4$ (Fig. 3), then the mean values of the deep vadose zone pore fluids (-14.4 ± 0.6 and -124 ± 4) are shifted relative to the inferred mean precipitation values by $+3.6 \pm 0.8$ ‰ and $+14 \pm 6$ ‰. The deep vadose zone waters are therefore shifted

along a δD – $\delta^{18}O$ slope of about 4, which is close to that expected based on experiments (Allison and Barnes, 1983).

Near-Surface Value of $\delta^{18}O$

The isotopic effects caused by evaporative loss of water from unsaturated soils to the atmosphere have been extensively studied (Allison and Barnes, 1983; Barnes and Allison, 1983, 1984, 1988; Munnich et al., 1980; Zimmerman et al., 1967; Mathieu and Bariac, 1996). The $\delta^{18}O$ and δD values of surface moisture increase with progressive evaporation as a result of preferential loss of the light isotopomer ($H_2^{16}O$). Due to capillary effects and the relatively fast molecular exchange rates between soil water vapor and liquid, the isotopic effects caused by evaporation at the soil surface usually penetrate to a depth of only 0.5 to 3 m. The distance of penetration depends on the evaporation rate, the soil type, and the amount of time between infiltration events (Barnes and Allison, 1988; Mathieu and Bariac, 1996). In sandy soils, where the uppermost 10 cm or more can dry out in a few months, the maximum $\delta^{18}O$ value that develops in the soil water is found at the bottom of the dry-out zone (Allison and Barnes, 1983).

As the water content of the near-surface soil decreases from evaporation, capillary forces cause upward movement of deeper water toward the surface, which limits the isotopic enrichment at the surface. The limiting steady-state value of delta at the surface (or at the bottom of the vapor phase transport zone) can be calculated from the expression for the isotope ratio ($R_i = {}^{18}O/{}^{16}O_i$), which is given by (Allison and Barnes, 1983)

$$R_{max} = \alpha_{eq}[(1 - h_a)\alpha_{kin}R_p + h_aR_a] \quad [1]$$

where R_{max} is the maximum surface or near surface ratio (${}^{18}O/{}^{16}O$ or D/H), R_p is the ratio in infiltrating precipitation, R_a is the average ratio in the atmosphere, and h_a is the average relative humidity of the air. The α_{eq} parameter is the equilibrium ratio of isotopic ratios between water and air at the average temperature of the site, and α_{kin} is the kinetic fractionation factor associated with evaporation under nonequilibrium conditions. The kinetic factor is dependent on wind speed (Merlivat, 1978a) and can be expressed as $\alpha_{kin} = (D_o^{vap}/D_i^{vap})^n$, where $n \approx 0.2$ for direct evaporation to the atmosphere and $n \approx 0.6$ to 1.0 for diffusion through porous soil. In this expression D_o^{vap} is the molecular diffusion coefficient for the light isotopomer of water ($H_2^{16}O$) in air, and D_i^{vap} is the molecular diffusion coefficient for the heavier isotopomer ($H_2^{18}O$ or HDO). The diffusion coefficient values used for calculating α_{kin} for H_2O/HDO are determined by Merlivat (1978b) and differ from the values that would be predicted based on kinetic theory due to surface cooling effects (Cappa et al., 2003). For the summer conditions at Hanford, the value of α_{eq} can be taken to be 1.0097 for ${}^{18}O/{}^{16}O$ (corresponding to $T \approx 20^\circ C$), and the value of α_{kin} is 1.0065 for evaporation directly to the atmosphere and between 1.014 and 1.028 for vapor phase diffusion through dry porous soil (Mathieu and Bariac, 1996).

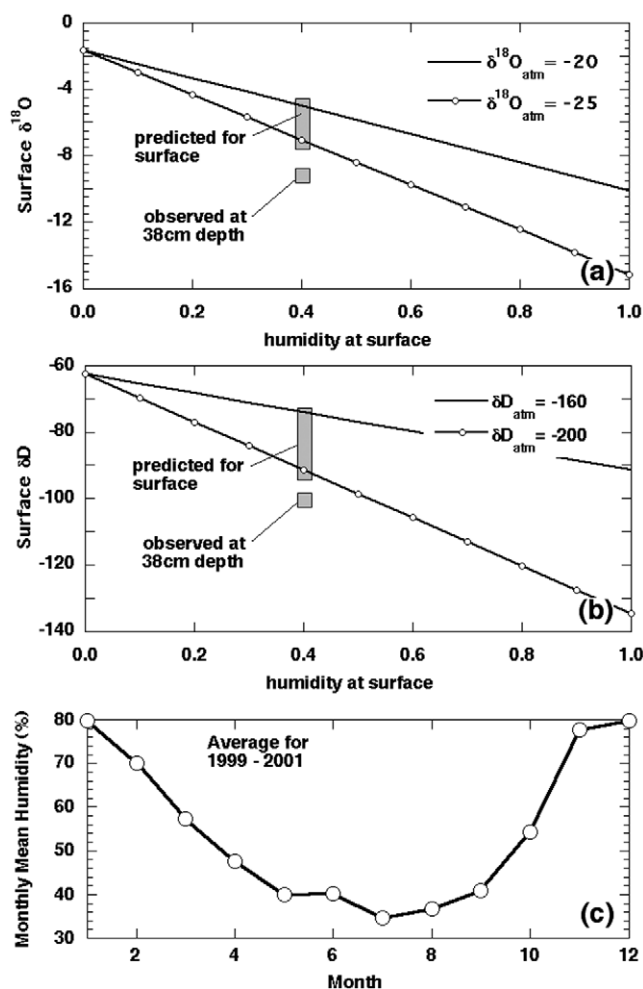


Fig. 5. Predicted relationship between (a) the maximum $\delta^{18}O$ of near surface soil water and atmospheric relative humidity and (b) the δD of near surface soil water and atmospheric relative humidity for $T = 20^\circ C$. The curves give the surface value in a saturated soil column using the equation given by Barnes and Allison (1983). For soil columns that dry out, the maximum value occurs below the surface and can be somewhat different from that shown (Barnes and Allison, 1988; Mathieu and Bariac, 1996). The values measured for the sample from the 38-cm depth in the W22-48 core are reasonably consistent with the local conditions (summer relative humidity of 40% and mean winter precipitation values of $\delta^{18}O = -18$ and $\delta D \approx -138$). (c) Monthly mean humidity at the Hanford weather station (<http://etd.pnl.gov:2080/HMS/>) for 1999 through 2001.

Figures 5a and 5b show the relationship between the predicted value of $\delta^{18}O_{max}$ and δD_{max} and atmospheric relative humidity, using the direct evaporation kinetic factors and a range of possible values of the atmospheric water vapor value of $\delta^{18}O$. The atmospheric values for $\delta^{18}O$ are estimated assuming that the summer water vapor is about 10‰ lower than typical summer precipitation values (-10 to -15), and δD is equal to $8\delta^{18}O$ (this puts the values off of the GMWL by about -10% in δD , as is observed for the typical summer precipitation). The mean humidity in the summer months (May–October) in this locality is quite close to 40%, and the monthly averages are fairly constant from May to September (Fig. 5c; Hanford weather station data from <http://etd.pnl.gov:2080/HMS/>). The measured values of both $\delta^{18}O$ and δD at 38 cm depth (-9.1 , -100), which

are 9 and 38‰ higher than the precipitation values, are lower than the values calculated for the surface at 40% humidity ($\delta^{18}\text{O} = -5$ to -7 and $\delta\text{D} = -74$ to -92). The differences are reasonably consistent with the theory since the values at 38 cm should be lower (Fig. 7).

Model for Deep Vadose Zone $\delta^{18}\text{O}$

This section describes a model developed to account for the isotopic properties of the deep vadose zone pore fluids. The pore fluids throughout the approximately 70-m vadose zone section average $\delta^{18}\text{O} = -14.4\text{‰}$, which is about 3.6‰ higher than the value we infer for average winter precipitation (Fig. 3 and 4). Both the shift relative to precipitation values and the uniformity of the subsurface values are significant. The shift relative to precipitation values must be related to the way that evaporation affects the water moving through the uppermost 1 to 2 m of the section (Allison and Barnes, 1983; Barnes and Allison, 1988). The evaporation effects that originate in the near-surface zone are apparently preserved when the shallow water is displaced downward by subsequent infiltration events. If simple plug flow described the downward water transport, then the deeper waters would be expected to show a sawtooth pattern of $\delta^{18}\text{O}$ vs. depth. That this is not observed suggests that dispersion is large enough to remove the oscillations during downward transport.

The model presented here is semiquantitative and applies strictly only to unvegetated sites. It shows that the deep vadose zone values of $\delta^{18}\text{O}$ and δD depend on the precipitation $\delta^{18}\text{O}$ and δD values, the water retention properties of near surface soils, the total amount of infiltration during the wet season, and the average relative humidity and evaporation rate during the dry season. The model predicts that deep drainage in an environment such as that at Hanford, with low, seasonal precipitation, invariably leads to deep vadose zone fluids that show significant isotopic effects of evaporation and therefore are not representative of wet season precipitation. The model also allows us to evaluate the conditions necessary for recharge water to approximate the precipitation isotopic values rather than be shifted to higher delta values. Barnes and Allison (1988) proposed a semi-empirical model relating the isotopic shift of deep vadose zone water (relative to average precipitation) and the annual net infiltration rate. Matheiu and Bariac (1996) presented a more general numerical model. The analysis here employs some of the features of these previous models. In general, models that attempt to account for the isotopic composition of deep vadose zone waters are not simple and require approximations.

Diffusivity of Water in Unsaturated Soil

The isotopic composition of deep vadose zone waters is determined by the isotopic characteristics of the soil moisture in the near surface, which in turn can be described with two parameters—a maximum isotopic shift and a length scale for the attenuation of this shift with depth in the soil (Barnes and Allison, 1988). The maximum isotopic shift is limited by the local atmospheric

vapor isotopic composition and the relative humidity (Eq. [1]). The $\delta^{18}\text{O}$ vs. depth profile in the upper 1 to 3 m soil below the vapor phase transport region is expected to be approximately exponential, with a characteristic length L , which increases with time after an infiltration event to a steady-state value of

$$L \approx \frac{\theta}{E} \left[D_o^{\text{liq}} \tau + D_o^{\text{vap}} \tau' \frac{(\phi - \theta) \rho_{\text{vap}} C_{\text{sat}}}{\theta \rho_{\text{liq}}} \right] \quad [2]$$

where the first term in brackets is the effective diffusivity of liquid water isotopes through the soil water, and τ is the tortuosity factor for liquid water. The term E/θ is the pore velocity of the water moving upward to balance evaporation from the surface at the rate E , and θ is the average water content (averaged over time and depth) during the time period where evaporation is the main process affecting the soil moisture. The specification of an effective θ value for drying soil requires approximations and is discussed further below. The second term in brackets is the vapor phase diffusion contribution to isotopic redistribution in the soil water. Vapor phase transport is substantial when saturation is low as in sand and gravel. The vapor phase diffusion term includes the ratio of densities of water vapor and liquid water, the air-filled pore space ($\phi - \theta$), the saturation mixing ratio (mole fraction) of water in air (C_{sat}), and the tortuosity factor for water vapor (τ'). The formulation for vapor diffusivity has been used in the previous treatments of soil moisture evaporation (Barnes and Allison, 1988; Mathieu and Bariac, 1996). Assuming D_o^{liq} at 20°C to have a value of $2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\tau = \tau' = 0.6$, and $\phi = 0.38$, the term in brackets takes on values between 560 and 3000 $\text{cm}^2 \text{ yr}^{-1}$ for $\theta = 0.2$ to 0.02. At low values of θ/ϕ , vapor phase transport is relatively large in comparison to the total water content of the soil.

Estimation of Evaporation Rates in Hanford Soils

Based on Eq. [2], the length scale L depends strongly on the evaporation rate. Theoretically, the evaporation rate should depend on the soil water content, so θ and E are not independent. To estimate evaporation rates and relate them to soil water contents at Hanford, we start with a model proposed by Gee and Ward (2002), which yields a relationship between the fraction of fine material (grain size $< 53 \mu\text{m}$) in Hanford soils and the annual water loss due to evaporation from the soils (the evaporation factor E_f ; Fig. 6a). In Fig. 6b we provide rough estimates of maximum winter and minimum late summer water contents of soils as a function of the percentage of fines. Figure 6c plots the mid-point water content from Fig. 6b against the evaporation factor formulation of Gee and Ward (2002) from Fig. 6a. The near-linear relationship suggests that it is possible to formulate the evaporation rate as

$$E(\theta, h_a) \approx E_o(1 - h_a)(\theta - \theta_o), \quad [3a]$$

where E is the evaporation rate, E_o is a reference evaporation rate, which is applicable to the soil being investigated and reflects the typical conditions of temperature and wind speed at the location, θ_o is a constant, and h_a

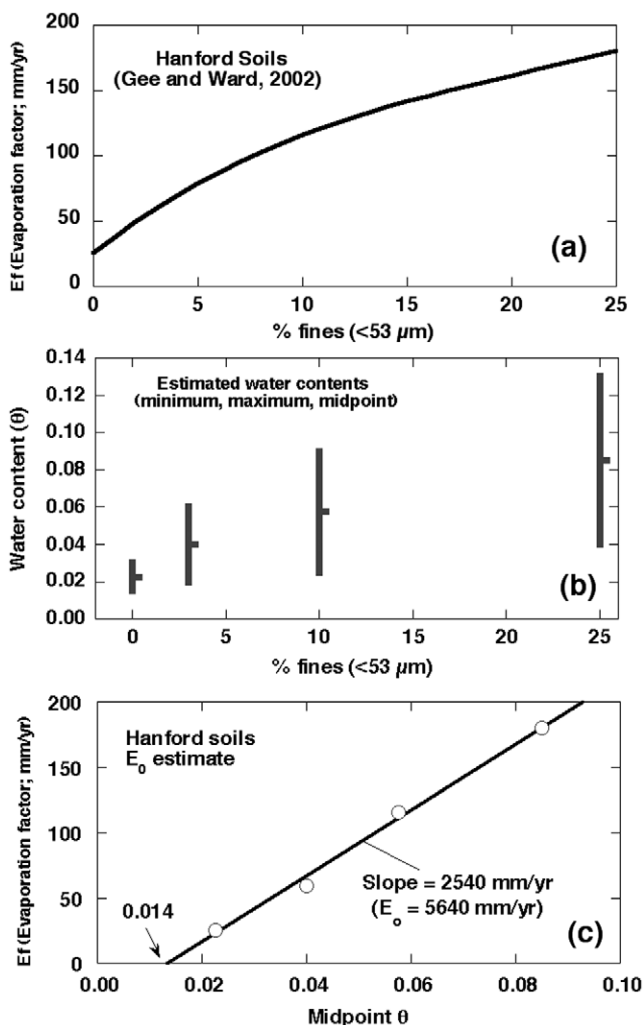


Fig. 6. (a) Measured evaporation factor (E_f) vs. percentage fine material (<53 μm) for Hanford soils as determined by Gee and Ward (2002). The E_f value is an estimate of annual water loss by evaporation. (b) Estimated water content range and midpoint for Hanford soils as a function of percentage of fine material in the soil. The maximum values apply to the winter wet season and the minimum values, which are reached only by the upper 50 cm or so of the soil, apply to late summer. (c) Evaporation factor vs. the midpoint water content value from Fig. 6b. The slope of the line and the x -intercept represent the values used for $E_o(1 - \bar{h}_a)$ and θ_o (Eq. [4b]).

is humidity. Equation [3a] can be used to express the evaporation factor as

$$E_f = E_o \int_{t=0}^{t=1\text{yr}} [1 - h_a(t)][\theta(t) - \theta_o] dt \approx E_o(1 - \bar{h}_a)(\bar{\theta} - \theta_o) \quad [3b]$$

If we take the midpoint water content values of Fig. 6b as approximations for $\bar{\theta}$, then the relationship in Fig. 6c gives $E_o(1 - \bar{h}_a) = 2540 \text{ mm yr}^{-1}$ and $\theta_o = 0.014$. Using the mean annual humidity at the Hanford weather station ($h_a = 0.55$; see Fig. 5c) gives $E_o = 5640 \text{ mm yr}^{-1}$. Equation [3a] provides a means of estimating evaporation rate for Hanford soils as a function of humidity and water content that is at least roughly calibrated with the data of Gee and Ward (2002).

Denoting the term in brackets in Eq. [2] as D^* , then

$$L \approx \frac{D^*\theta}{E_o(1 - h_a)(\theta - \theta_o)} \quad [4a]$$

Using $E_o = 5640 \text{ mm yr}^{-1}$, Eq. [4a] gives a range for L of about 1.8 to 30 cm for values of θ between 0.2 and 0.02. The time required to reach the steady state is approximately L^2/D^* , which is 1.5 d to 3 mo for the parameters chosen. L is likely to be larger than 1.8 to 30 cm because the evaporation rate is controlled by the soil moisture content near the surface, which should be significantly lower than the water content deeper in the soil below the dry-out zone, which will largely determine $D^*\theta$. To account for this in the model, Eq. [4a] is modified to

$$L \approx \frac{D^*\theta}{E_o(1 - h_a)(\theta_s - \theta_o)} \quad [4b]$$

where $\theta_s = 0.50$. θ_s is the water content in the dry-out zone and θ is the water content below. The choice of a factor of 0.5 to relate the near surface water content to the deeper water content is reasonable based on the typical range of water contents for Hanford soils between the wet and dry seasons (Fig. 6b) and the experiments of Allison and Barnes (1983). Equation [4b] yields L values of 2.7 to 32 cm for θ_s in the range 0.2 to 0.02, and the corresponding time to reach steady state is about 6 d to 8 mo. Note that D^* also depends on θ .

Late Summer Soil Isotopic Profile and Deep Vadose Zone $\delta^{18}\text{O}$

The simplified model we consider here assumes there is infiltration during the wet season with relatively little evaporation, followed by an extended period of evaporation accompanied by continued downward advection of some water. The resulting isotopic profile in the uppermost meter or so of soil is diagrammed schematically in Fig. 7. At the end of the dry season the mean isotopic composition of the newly infiltrated water, in delta units, is described by

$$\delta_{\text{mean}} \approx \delta_p + (\delta_{\text{max}} - \delta_p) \int_{L_v}^{L_{\text{in}}} \frac{\exp[-(z - L_v)/L]}{L_{\text{in}}} dz + [0.5(\delta_{\text{max}} + \delta_s) - \delta_p] \frac{L_v}{L_{\text{in}}} \quad [5]$$

where L_{in} is given by q_{net}/θ , L_v is the thickness of the dry-out zone at the top of the soil column, and θ is the final mean water content of the soil at the end of the dry season. The mean value of $\delta^{18}\text{O}$ as represented by Eq. [5] should be preserved in the deeper part of the vadose zone section as continuing infiltration displaces this near surface water to greater depth. For a given soil type (and θ value), the $\delta^{18}\text{O}$ shift of vadose zone waters should vary approximately as $1/q_{\text{net}}$, where q_{net} is the yearly recharge or "deep drainage."

Model Limitations and Uncertainties

The main uncertainty in this approach for relating $\delta^{18}\text{O}$ and net infiltration is the estimation of L , which in turn is sensitive to the formulation for the evaporation

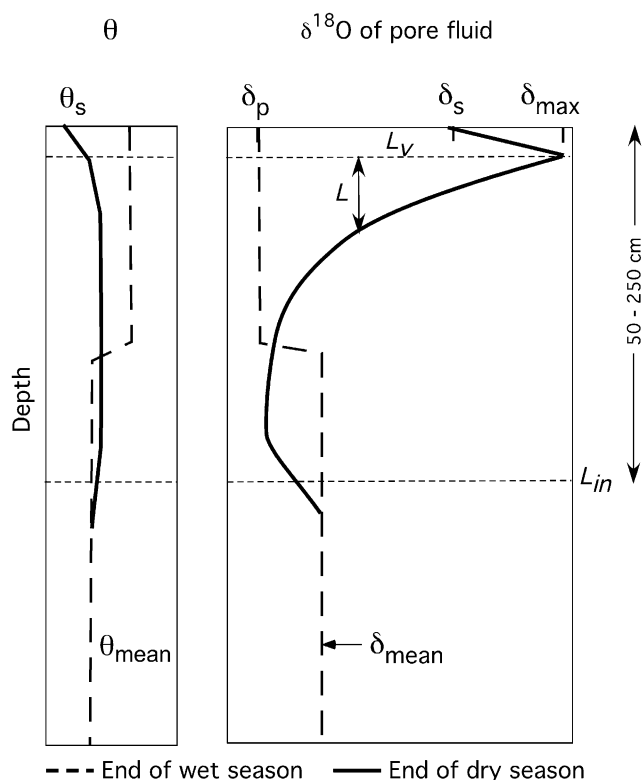


Fig. 7. Conceptual model for the origin of heavy $\delta^{18}\text{O}$ values in deep vadose zone fluids. Initial infiltration involves water with the $\delta^{18}\text{O}$ value characteristic of local winter precipitation ($=\delta_p$) and results in moisture and $\delta^{18}\text{O}$ profiles shown by the dashed lines. By the end of the summer dry season (solid lines in figure), evaporation has produced isotopic enrichment of the water in the uppermost meter or so of the soil column. The enrichment is accompanied by partial dry-out of the soil to a depth L_v , and continued downward drainage to a depth L_m . Subsequent displacement of the enriched waters by the next year's infiltration, coupled with dispersion generates a relatively uniform $\delta^{18}\text{O}$ value in the deep vadose zone fluids (δ_{mean}) that represents the mean isotopic composition of the water that initially resided between the surface and the depth L_m .

rate E . The net isotopic shift of the deep vadose zone fluids relative to that of infiltrating precipitation is roughly proportional to L/L_{in} . In principle L can be measured by sampling the upper meter of soil in late summer, so it should be possible to calibrate the model with appropriate data. Barnes and Allison (1988) noted that measured values of L in soils from arid regions were typically larger than predicted with Eq. [2]. They asserted that this might be explained by enhanced vapor phase diffusion. Barnes and Allison (1988) also argue that the isotopic shift should vary as $(1/q)^{1/2}$, which will be the case if the time between infiltration events is short in comparison to the amount of time needed to establish a steady state isotopic profile.

The calculation of the length L assumes no downward drainage of soil moisture during evaporation (Barnes and Allison, 1988). If there is continued downward drainage of soil moisture, the length scale of the isotopic effects may be increased. For Hanford, the wetting and drying of soils occurs roughly on an annual cycle, and there are about 6 to 7 mo each year when rainfall is small, relative humidity low, and there is essentially no infiltra-

tion (Gee et al., 1992; Fayer et al., 1999; Tyler et al., 1999). Except for clean gravels with very low water contents, the soil isotopic profile should reach steady state soon after the end of the infiltration season. Then the depth of penetration of the evaporation effects will lengthen during continued drainage accompanied by slowing evaporation at decreasing moisture content. The coupled processes and time dependence of the water content and isotopic evolution can be fully captured only by a numerical model. In the simple model we have tried to capture the maximum isotopic shift by using the soil water contents typical of the late summer dry season.

Vegetation is not expected to affect the isotopic composition of soil water, as plant roots remove water from the soil with little isotopic fractionation (Dawson and Ehleringer, 1993; Thorburn et al., 1993). However, the presence of vegetation changes the relationship between $\delta^{18}\text{O}$ of vadose zone waters and recharge. The estimation of recharge via Eq. [3] above gives a maximum value if the site is vegetated. The actual value of net infiltration would be lower by an amount equal to the annual evapotranspiration moisture flux.

Model Results and Parameter Sensitivity

The calculated relationships between the isotopic composition of deep vadose zone pore waters and net infiltration are summarized in Fig. 8 for the model described above as applied to Hanford soils. The following input parameter values were used for the calculation: $E_o = 5640 \text{ mm yr}^{-1}$, $h_a = 0.4$, $\alpha_{\text{kin}} = 1.0065$, $\phi = 0.38$. The value of L_v is set so that the diffusive flux of water vapor through the layer between the surface and depth L_v matches the evaporation rate calculated from Eq. [3], assuming that at depth L_v the relative humidity in the soil vapor is 1.0. The value of $\delta^{18}\text{O}_{\text{max}}$ is approximated as $\delta^{18}\text{O}_s + 0.1L_v$, where L_v is given in centimeters, and $\delta^{18}\text{O}_s$ is given by Eq. [1] using the above quoted value of α_{kin} . The soil water content, θ_s , is assumed to apply to a depth L_v , and the water content between depths L_v and L_{jin} is assumed to be $\theta = 2\theta_s$.

The model predicts that the $\delta^{18}\text{O}$ shift of deep vadose zone waters, relative to values in the infiltrated winter precipitation, should increase with decreasing net infiltration (Fig. 8). In addition, coarser soils, with lower moisture contents, should have larger isotopic shifts than finer soils for the same amount of annual drainage. For unvegetated soils, net infiltration is correlated with the percentage of fine material in the soil (Gee and Ward, 2002) and hence with θ_s . Because of this relationship, there may be little dependence of $\delta^{18}\text{O}$ on net infiltration, at least for soils with low contents of fine material ($\leq 10\%$). Typical values for deep vadose zone fluids should be in the range $\delta^{18}\text{O} = -13$ to -15 for net infiltration fluxes of 30 to 100 mm yr^{-1} . Finer grained soils, which should have low net infiltration, could produce larger $\delta^{18}\text{O}$ shifts. Overall, the model suggests that all recharge through the vadose zone in a relatively arid environment like the Hanford area is likely to be shifted in $\delta^{18}\text{O}$ relative to winter precipitation by $+2$ to $+6\%$.

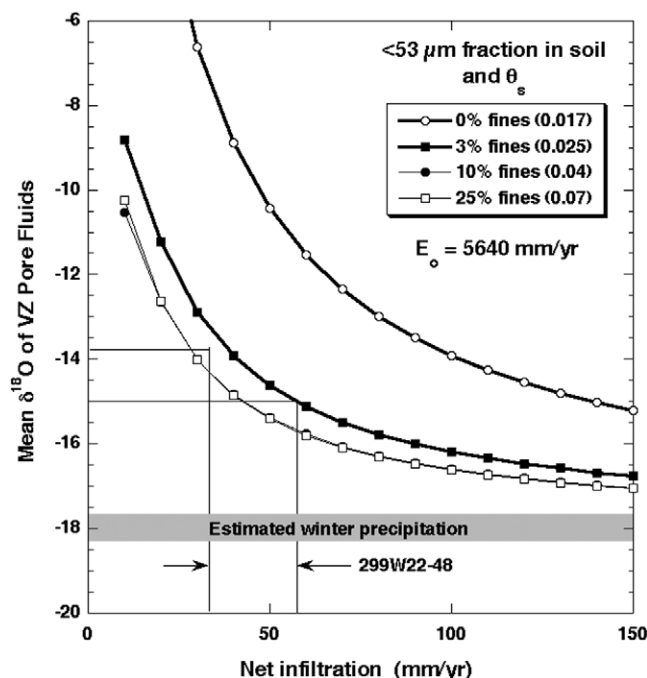


Fig. 8. Predicted relationship between annual net infiltration and the $\delta^{18}\text{O}$ of deep vadose zone waters, for soils with different water retention characteristics. The curves shown represent the solution to Eq. [5] for soils with different contents of fine material ($<53\ \mu\text{m}$), using the minimum water contents from Fig. 6b (θ ; given in parentheses in the legend), and for $h_a = 0.4$, $T = 20^\circ\text{C}$, and $E_0 = 5640\ \text{mm yr}^{-1}$. The percentage of fine material corresponds approximately to the following soil types (0%: gravel; 3%: coarse sand; 10%: sand; 25%: sandy loam). The horizontal lines denote the mean and standard deviation of measured $\delta^{18}\text{O}$ values for vadose zone water at the 299W-22-48 site (Table 1 and Fig. 4; average = -14.4 ± 0.6). The data correspond to a net infiltration flux in the range 35 to 60 mm yr^{-1} .

and this conclusion would apply to vegetated as well as unvegetated areas.

The results of the model are quite different from the model proposed by Barnes and Allison (1988). Their model was that deep infiltration is related to the δD shift according to $D = 20/q^{1/2}$, where D is the δD shift in per mil, and q is the deep infiltration in millimeters per year. Assuming that $^{18}\text{O} = 0.25D$, the equivalent equation for $\delta^{18}\text{O}$ is $^{18}\text{O} = 5/q^{1/2}$. Hence the Allison and Barnes model predicts that a $\delta^{18}\text{O}$ shift of 3.6‰ corresponds to a net infiltration flux of about 2 mm yr^{-1} , about 25 times smaller than predicted by the model proposed in the current work. Net infiltration fluxes of 30 to 100 mm yr^{-1} are predicted to produce $\delta^{18}\text{O}$ shifts of 0.5 to 1‰ in the Allison and Barnes model.

The curves shown on Fig. 8 are reasonably sensitive to the choice of value for E_0 . For example, if E_0 is changed $\pm 2000\ \text{mm yr}^{-1}$ from the specified value of 5640 mm yr^{-1} , the curves shift by $\pm 0.8\text{‰}$ for 50 mm of net infiltration. The predicted $\delta^{18}\text{O}$ values are not sensitive to the details of the water content profile because of offsetting effects on L_{in} and D^* . The results are insensitive to the value used for humidity (h_a) in the range 0.3 to 0.6 ($\pm 0.1\text{‰}$ for this range for $q = 50\ \text{mm yr}^{-1}$), and the assumed $\delta^{18}\text{O}$ of atmospheric moisture ($\pm 0.1\text{‰}$ for $\delta_{\text{atm}} = -20$ to -25 and $q = 50\ \text{mm yr}^{-1}$).

The calculation of L_v is done primarily to establish the value of $\delta^{18}\text{O}_{\text{max}}$. The model results are not sensitive to changes in the value of L_v except at low net infiltration fluxes. In any case the model is not accurate at low net infiltration fluxes because the approximations made are not sufficiently good when L_{in} becomes so small that it approaches the value of L , which happens when net infiltration is $<20\ \text{mm yr}^{-1}$.

Net Infiltration Flux (Drainage) for 299-W22-48

The $+3.6 \pm 0.8\text{‰}$ shift of vadose zone pore fluids at the 299-W22-48 site relative to winter precipitation is shown with horizontal lines in Fig. 8. The near surface soil at this site has some fine material, and based on the sample at the 0.38-m depth we assume $\theta \approx 0.07$. So the 3.6‰ shift corresponds to a net infiltration rate in the range 35 to 60 mm yr^{-1} . If the effects of vegetation are included, which would lower net infiltration without changing $\delta^{18}\text{O}$, the 3.6‰ shift could correspond to net infiltration rates lower than 35 mm yr^{-1} . The model allows the $\delta^{18}\text{O}$ values to be used only to infer a maximum net infiltration flux, which would apply in the absence of vegetation and hence may be applicable to this site and many others at Hanford. The $\delta^{18}\text{O}$ values of vadose zone pore waters at Hanford are not likely to be shifted by more than about 6 to 7 units unless there is virtually zero net infiltration for a long time period (order 10 000 yr).

Walvoord et al. (2001) reported $\delta^{18}\text{O}$ values of vadose zone pore fluids from Nevada that showed large $\delta^{18}\text{O}$ shifts that decreased steadily from the surface to a depth of 25 m. The pattern was interpreted as resulting from an extended period of water loss by vapor and liquid phase diffusion and requires that there be zero infiltration. The pattern observed by Walvoord et al. (2001) is not what is observed at the 299-W22-48 site. The pattern we observe is generated by a significant amount of deep drainage, most likely in the range 30 to 100 mm yr^{-1} . Such values of deep drainage are far above the values inferred for vegetated sites on the Hanford Plateau based on Cl^- mass balance measurements (Murphy et al., 1996), but within the range of estimates based on other data (Gee et al., 1992).

As noted above, the 299-W22-48 site was probably vegetated until about 50 yr ago. It is possible, therefore, that until the vegetation was removed there was lower net infiltration and that it increased starting in the 1950s. If there had been 35 to 60 mm yr^{-1} of net infiltration over 50 yr, with average moisture content of 9% by volume, the wetting front would have penetrated to a depth of 20 to 33 m. This model is consistent with the isotopic data in the depth range 0 to 33 m. The similar $\delta^{18}\text{O}$ values below 33 m could still be consistent with lower net infiltration fluxes (caused by vegetative removal of water with no isotopic fractionation) as long as there was still a significant amount of deep infiltration. High net infiltration over the past 50 yr would help explain the somewhat elevated tritium and water contents down to 30 to 35 m (Table 1 and Fig. 2).

Strontium isotopic data from this site have been inter-

puted to be reflective of a long-term (100–1000 yr) average net infiltration flux of about $10 \pm 3 \text{ mm yr}^{-1}$ (Maher et al., 2003). The Sr data are unlikely to have been disturbed by recent vegetation removal due to the long memory afforded by the reservoir of adsorbed Sr in the soil. Hence, the combined Sr and O isotopic data suggest that the long-term natural recharge at the site is about 10 mm yr^{-1} , and the removal of vegetation may have increased the recharge to levels of about 50 mm yr^{-1} in the last 50 yr.

Age of Laterally Transported Water

The water currently found at this site at a depth of 44 m must have been transported laterally to the site. Based on the results of injection experiments (Ward et al., 2000), the water currently found in the fine-grained upper Cold Creek unit may have initially moved laterally in the coarser sediments just above, and has since moved downward into the fine-grained layers. The inferred lateral transport must have occurred recently, because the isotopic distinction of this layer of water should be lost by exchange with surrounding layers by liquid and vapor phase diffusion. The time required to degrade the isotopic signal depends on the thickness of the isotopically distinct layer and the water content, as well as on the effective diffusivity if the redistribution is controlled by diffusion, or the dispersivity if redistribution is primarily caused by advective dispersion. For a standard diffusion model of a layer of thickness $2a$, the time required to degrade the maximum signal by 10% is given by $0.1a^2/D^*$ for uniform water content as a function of depth. For $a = 100 \text{ cm}$ and $D^* = 500 \text{ cm}^2 \text{ yr}^{-1}$, this gives $t = 20 \text{ yr}$. If the advective velocity is order 0.1 to 0.5 m yr^{-1} , the dispersion coefficient is likely to be similar in magnitude to D^* and hence a similar amount of time is required to degrade the signal. The estimate of approximately 20 yr is not precise, since we do not have the thickness or shape of the isotopically anomalous layer well defined, and the variation in sediment water content near the isotopic anomaly also complicates the calculation somewhat. Nevertheless, the resultant value for the age is clearly consistent with the idea that this intruding water is a result of recent (since 1945) site activities.

Implications for Groundwater $\delta^{18}\text{O}$ Values

The model presented here implies that most if not all recharge in semiarid regions should be enriched in ^{18}O and D/H relative to the initial infiltrating precipitation, which implies that groundwater typically has $\delta^{18}\text{O}$ and δD values that do not directly reflect the values of precipitation in the recharge area. This conclusion is different from the normal assumption that groundwater delta values are very close to those of mean local precipitation (e.g., Gat, 1996). The model can be used to explore what conditions would produce minimal changes in $\delta^{18}\text{O}$ and δD during recharge and thus allow groundwater delta values to approximate those of precipitation. One obvious situation is when both initial infiltration and recharge are much larger than in the semiarid climate of

the Hanford site. As shown in Fig. 8, when net infiltration is greater than 150 mm yr^{-1} , the shift in $\delta^{18}\text{O}$ is typically less than 1 unit for all but the clean gravels. However, another strong determinant of the isotopic shift is the total porosity (ϕ). For the calculation of Fig. 8 we have used a value of 0.38 typical of granular materials. In fractured crystalline rocks, the effective porosity may be closer to the fracture porosity, which can be much smaller than 0.38. In the case of fractured rocks, infiltrating water can penetrate to relatively great depth during the wet season, and then may not be significantly affected by evaporation during the dry season. Using the model as a rough guide, the predicted shift of approximately $+1.0$ to $+2.8\%$ in $\delta^{18}\text{O}$ for 150-mm recharge with $\phi = 0.38$ (Fig. 8) changes to only $+0.3$ to $+1.0$ for $\phi = 0.1$ ($\theta_s = 0.017\text{--}0.04$), with no other changes in the model parameters. The primary effect of decreasing ϕ is to increase L_{in} and to decrease D^* . To treat fractured rocks in detail, the model would also need to take account of the partitioning of moisture between the fractures and the matrix, which it does not.

The overall conclusion is that under conditions of recharge through fractured crystalline rocks, or for high recharge rates, the shift of $\delta^{18}\text{O}$ during percolation through the vadose zone may be $<1\%$ and therefore difficult to establish due to the seasonal variability of precipitation values. The fact that wet season precipitation in semiarid regions tends to have $\delta^{18}\text{O}$ values that are lower than the annual average would also offset the evaporation effects and help make the groundwater $\delta^{18}\text{O}$ values close to the values for average precipitation.

CONCLUSIONS

The O and H isotopic data presented show that the natural pore fluids currently occupying the thick vadose zone region under the Hanford Plateau are shifted to higher $\delta^{18}\text{O}$ and δD relative to mean wet season precipitation. The pore fluids at the 299-W22-48 well site, just east of the S-SX tank farm, are fairly uniform as a function of depth, with an average shift of $\delta^{18}\text{O}$ of about $+3.6\%$ relative to typical groundwater and winter precipitation values, and about $+2.5\%$ relative to average Columbia River water values. The distinct isotopic composition of the ambient vadose zone fluids implies that industrial water, which is derived from the Columbia River, contains a natural tracer in its $\delta^{18}\text{O}$ value and hence that $\delta^{18}\text{O}$ measurements can be used to identify subsurface water that comes from leaking pipes or from large volume water releases at the surface. The isotopic composition of water infiltrating from an evaporation pond may not be as distinctive unless it has $\delta^{18}\text{O}$ that is higher than the typical vadose zone water.

A model is developed to attempt to explain the relatively large and nearly uniform shift of deep vadose zone pore fluids in $\delta^{18}\text{O}$. The model describes approximately how evaporation affects water that infiltrates the upper 1 to 3 m of soil during the relatively wet, cool, and humid winter months and then is modified by evaporation and drainage during the dry summer months. The model shows that under most conditions likely to

apply at Hanford, vadose zone fluids derived from infiltration through bare surface soils should be shifted to $\delta^{18}\text{O}$ values that are 2 to 6 units higher than the infiltrating winter precipitation. This shift is dependent on both net infiltration flux and soil water retention characteristics. The model does not account for the effects of plants, which decrease recharge without substantially affecting $\delta^{18}\text{O}$, and hence the $\delta^{18}\text{O}$ value of vadose zone fluids can give only a maximum value for the recharge flux for vegetated sites.

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